THEORETICAL CHEMISTRY INSTITUTE

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WIS-TCI-13 Series 3

15 May 1963

MADISON, WISCONSIN

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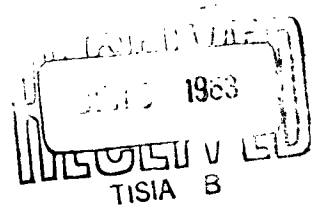
## ABSTRACT

The explicit solutions of the first-order perturbation equations for a one dimensional system can be obtained by quadratures provided that the zeroth-order wave function does not have any nodes. Methods of integrating the equations are developed for excited states where the zeroth-order wave function has nodes. One of these methods is suitable for obtaining numerical solutions.

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* This research was supported jointly by the following contract and grant: United States Air Force Contract AF 33(657)-7311 and National Aeronautics and Space Administration Grant NsG-275-62(4180).

# THE INTEGRATION OF THE FIRST-ORDER PERTURBED WAVE EQUATION FOR EXCITED STATES OF ONE DIMENSIONAL SYSTEMS

## Introduction

Recently there has been a renewed interst in perturbation theory in quantum mechanics. One aspect of this development, due largely to Dalgarno and his colleagues[1], has been the successful calculation of the first-order corrections to the expectation values of one-electron operators. This has been achieved by obtaining the exact solutions of the first-order wave equations rather than by attempting to use the very awkward representation of the first-order wave function in terms of the spectrum of solutions of the unperturbed hamiltonian.

It was first pointed out by Young and March[2] that the first-order wave equation for a one dimensional system can always be integrated by quadrature. However these authors only discussed the ground state of the system in which the wave function has no nodes. In the case of excited states singularities occur in the equation owing to the nodes of the unperturbed wave function. The object of this paper is to show how the singularities may be handled both analytically and in numerical work.

## First-Order Wave Equations

For a system with the hamiltonian

$$H = H_o + V$$

the perturbation expansions of the exact wave function $\psi_n$ and the exact energy $E_n$ of the nth state may be written

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[1] A. Dalgarno, "Quantum Theory" edited by D. R. Bates, (Academic Press, New York, 1961), Vol. I, Chapter 5; A. Dalgarno, "Advances in Physics" (Phil. Mag. Supplement) 11, 281 (1962); C. Schwartz, Annals of Phys. 2, 156, 170, and 176 (1959).

[2] W. H. Young and N. H. March, Phys. Rev. 109, 1854 (1958).

$$\psi_n = \psi_n^{(o)} + \psi_n^{(1)} + \cdots \quad , \tag{1}$$

$$E_n = E_n^{(o)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \cdots \quad , \tag{2}$$

where $\psi_n^{(o)}$ and $E_n^{(o)}$ are the nth normalized eigenfunction and eigenvalue (assumed non-degenerate) of the unperturbed hamiltonian $H_o$ given by

$$(H_o - E_n^{(o)})\psi_n^{(o)} = 0 \quad . \tag{3}$$

The equation for the first-order wave function $\psi_n^{(1)}$ is

$$(H_o - E_n^{(o)})\psi_n^{(1)} + (V - E_n^{(1)})\psi_n^{(o)} = 0 \quad , \tag{4}$$

and therefore the first-order energy is given by

$$E_n^{(1)} = \langle \psi_n^{(o)} V \psi_n^{(o)} \rangle \quad ,$$

$$= V_n \quad . \tag{5}$$

The second- and third-order energies are given in terms of $\psi_n^{(1)}$ by

$$E_n^{(2)} = \langle \psi_n^{(1)} (V - V_n) \psi_n^{(o)} \rangle \quad , \tag{6}$$

$$E_n^{(3)} = \langle \psi_n^{(1)} (V - V_n) \psi_n^{(1)} \rangle - 2E_n^{(2)} \langle \psi_n^{(1)} \psi_n^{(o)} \rangle \quad . \tag{7}$$

The expectation value of an operator L in the nth state of the perturbed system may be expanded into different orders:

$$\langle L \rangle_n = \langle \psi_n L \psi_n \rangle / \langle \psi_n \psi_n \rangle \quad ,$$

$$= L_n^{(o)} + L_n^{(1)} + \cdots \quad , \tag{8}$$

where

$$L_n^{(o)} = L_n = \langle \psi_n^{(o)} L \psi_n^{(o)} \rangle \quad , \tag{9}$$

$$L_n^{(1)} = 2 \langle \psi_n^{(1)} (L - L_n) \psi_n^{(o)} \rangle \quad . \tag{10}$$

It has been pointed out by Dalgarno that in cases where the complexity of the perturbation V makes the first-order equation (4) too difficult to solve explicitly, it may nevertheless be possible to solve the first-order equation

$$(H_o - E_n^{(o)}) \chi_n + (L - L_n) \psi_n^{(o)} = 0 \quad . \tag{11}$$

The first-order correction (10) may then be written in the form

$$L_n^{(1)} = 2 \langle \chi_n (V - V_n) \psi_n^{(o)} \rangle \quad . \tag{12}$$

The integral in (12) is usually tractable even if V contains two-electron terms (such as $1/r_{12}$), so that the correction is obtainable if (11) can be solved, which may be possible if L is a one-electron operator. The mathematical problem is therefore to solve one-electron first-order wave equations of the type (11).

Reduction of the First-Order Wave Equation

The device used to simplify (11) is to put

$$\chi_n = f_n \phi_n \quad , \tag{13}$$

where we have replaced $\psi_n^{(o)}$ by $\phi_n$ for convenience, and to note that

$$(H_o - E_n^{(o)}) f_n \phi_n = (H_o f_n - f_n H_o) \phi_n \quad , \tag{14}$$

so that (11) may be written

$$\left[H_o, f_n\right] \phi_n + (L - L_n)\phi_n = 0 \quad , \tag{15}$$

where the square brackets denote a commutator. This means that if, as usual,

$$H_o = -\tfrac{1}{2}\nabla^2 + U_o \tag{16}$$

where the unperturbed potential energy $U_o$ is a scalar, then (15) becomes

$$\left[\nabla^2, f_n\right]\phi_n = 2(L - L_n)\phi_n \quad . \tag{17}$$

If this equation is multiplied by $\phi_n$, which we shall assume to be real, it may be rearranged to give

$$\nabla \cdot (\phi_n^2 \nabla f_n) = 2\phi_n(L - L_n)\phi_n \quad , \tag{18}$$

which is equivalent to the Wronskian form

$$\nabla \cdot (\phi_n \nabla \chi_n - \chi_n \nabla \phi_n) = 2\phi_n(L - L_n)\phi_n \quad . \tag{19}$$

Since the usual boundary conditions are that $\phi_n$ and $\chi_n$ vanish at the boundaries, the boundary condition on $f_n$ is that

$$\phi_n^2 \nabla f_n = 0 \quad \text{on boundaries} \; . \tag{20}$$

Solution of the First-Order Wave Equation for One Dimension

For a one dimensional system described by a variable $x$ confined to the interval $(a,b)$, equation (18) becomes

$$\frac{d}{dx}\left(\phi_n^2 \frac{df_n}{dx}\right) = 2\phi_n(L - L_n)\phi_n \quad . \tag{21}$$

This may be integrated directly to give

$$\phi_n^2 \frac{df_n}{dx} = M_n(x) \tag{22}$$

where

$$M_n(x) = 2\int_a^x \phi_n(\xi)(L - L_n)\phi_n(\xi)d\xi \ , \tag{23}$$

and the constant of integration vanishes because of the boundary condition (20).

The same treatment may be applied to a three dimensional system described by spherical coordinates in which the operator $L$ depends only on $r$, and the unperturbed wave function is of the form

$$\phi_n(r,\theta,\varphi) = R_n(r)\Theta_n(\theta,\varphi) \ . \tag{24}$$

In this case $f_n$ depends only on $r$, and the equation (18) reduces to

$$\frac{d}{dr}(r^2R_n^2 \frac{df_n}{dr}) = 2r^2R_n(L - L_n)R_n \ , \tag{25}$$

which is of the same form as (21) and may be integrated directly from the lower limit $r = 0$ to give

$$r^2R_n^2 \frac{df_n}{dr} = P_n(r) \tag{26}$$

where

$$P_n(r) = 2\int_o^r s^2R_n(s)(L-L_n)R_n(s)\,ds \ . \tag{27}$$

(a) Ground state

For the ground state, say $n = 0$, in which the unperturbed wave function $\phi_o(x)$ does not possess any nodes between $a$ and $b$, (22) may be integrated immediately to give

$$f_o(x) = f_o(a) + \int_a^x \frac{M_o(\xi)}{\phi_o^2(\xi)}\, d\xi \quad , \tag{28}$$

as pointed out by Young and March. It should be noticed that this integration is not required explicitly if $\chi_o = f_o\phi_o$ is to be used in an integral such as (12). This is because

$$L_o^{(1)} = 2\int_a^b f_o\phi_o(V - V_o)\phi_o dx \tag{29}$$

may be transformed by partial integration to give

$$L_o^{(1)} = -\int_a^b \frac{df_o}{dx} W_o(x) dx \quad , \tag{30}$$

$$= -\int_a^b \frac{M_o(x)W_o(x)}{\phi_o^2(x)}\, dx \quad , \tag{31}$$

where

$$W_n(x) = 2\int_a^x \phi_n(\xi)(V-V_n)\phi_n(\xi)d\xi \quad . \tag{32}$$

In particular the second-order energy becomes

$$E_o^{(2)} = -\tfrac{1}{2}\int_a^b \left[W_o(x)/\phi_o(x)\right]^2 dx \quad . \tag{33}$$

The only point requiring special discussion in the radial case when $R_n(r)$ has no nodes is the behaviour of $f_n(r)$ at the lower limit $r = 0$. If $R_n(0) \neq 0$, then $f_n(0)$ is finite as long as $LR_n(r)$ does not go to infinity faster than $r^{-1}$ at the origin.[3] If $R_n(r) \simeq r^{\ell}$ at the origin, then $f_n(0)$ is finite as long as $LR_n(r)$ goes to zero as fast as $r^{\ell-1}$ at the origin. The formula corresponding to (31) in this case is

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[3] If $LR_n(r)$ goes to infinity even as fast as $r^{-2}$ at the origin, no serious difficulties are encountered. However, in this case $f_n(0)$ might be infinite. For example, if $LR_n(r)$ goes to infinity as $r^{-2}$ at the origin, then $f_n(0)$ contains a term $A \ln(r)$.

$$L_n^{(1)} = -\int_o^\infty \frac{P_n(r)\, Q_n(r)}{r^2 R_n^2(r)}\, dr \qquad (34)$$

where

$$Q_n(r) = 2\int_o^r s^2 R_n(s)(V-V_n)R_n(s)\, ds \quad . \qquad (35)$$

(b) Excited states

Consider the case in which the nth unperturbed eigenfunction $\phi_n(x) = \psi_n^{(o)}$ has $n$ simple zeros at $a_1, a_2, \cdots, a_n$ in the interval $(a,b)$. Then if the first-order wave function $\chi_n = \psi_n^{(1)}$ is well-behaved, the function $f_n(x)$ will have simple poles at $a_1, \cdots, a_n$. The direct integration of (22) to yield $f_n$ presents difficulties because $M_n(x)$ does not vanish in general at the zeros $a_j$. Similarly the integral for $L_n^{(1)}$ corresponding to (31), namely

$$L_n^{(1)} = -\int_a^b \frac{M_n(x)W_n(x)}{\phi_n^2(x)}\, dx \quad , \qquad (36)$$

is infinite if $\phi_n$ vanishes in the range $(a,b)$.

To avoid the difficulties raised by the singularities in (22) and (36), let us assume that $\phi_n$, $f_n$, $M_n$ and $W_n$ are analytic functions in the vicinity of the real interval $(a,b)$. Then equation (22) may be written

$$\frac{df_n(z)}{dz} = \frac{M_n(z)}{\phi_n^2(z)} \qquad (37)$$

and integrated from $a$ to $x$ along any contour $C$ which does not pass through the zeros of $\phi_n$:

$$f_n(x) = f_n(a) + \oint_a^x \frac{M_n(z)}{\phi_n^2(z)}\, dz \quad . \qquad (38)$$

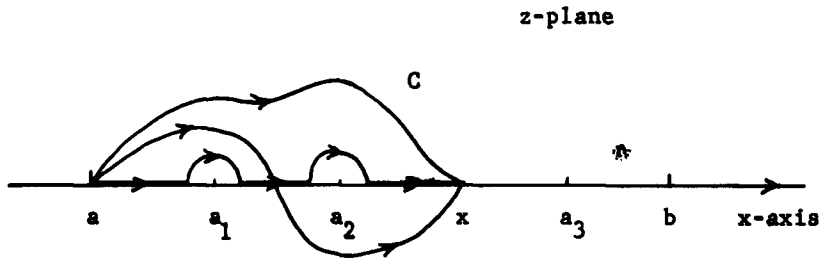


Figure 1.

By Cauchy's theorem C may be any of the contours connecting a and x shown in figure 1, since the integrand $M_n/\phi_n^2$ in (38) always has double poles at the points $a_1,\cdots,a_n$, and these do not contribute any residues to a contour enclosing them. The nature of the poles of $M_n/\phi_n^2$ follows from the simple character of the zeros of $\phi_n$ and the definition of $M_n$ by equation (23), according to which $M_n'(a_j) = 0$, and therefore in the vicinity of $a_j$

$$M_n(z) = M_n(a_j) + O(z-a_j)^2 \quad . \tag{39}$$

The same considerations apply to the integral expression for $L_n^{(1)}$ in equation (36), and the correct form is

$$L_n^{(1)} = -\oint_a^b \frac{M_n(z)W_n(z)}{\phi_n^2(z)}\,dz \tag{40}$$

where the path of integration C from a to b avoids the double poles at $a_1,\cdots,a_n$.

The radial case can be dealt with in the same way, and leads to the formula

$$L_n^{(1)} = -\oint_o^\infty \frac{P_n(z)Q_n(z)}{z^2R_n^2(z)}\,dz \quad . \tag{41}$$

It follows that when the integrations in (40) or (41) can be performed analytically it is unnecessary to consider the singularities explicitly, since formally it makes no difference whether one integrates along a contour with complex variable $z$ or along the real axis with variable $x$. To clarify the method and to illustrate the power of the integral formulae for excited states, it is useful to treat a simple example, for which we choose the polarizability of a particle in a one-dimensional box.

(c) Example

Consider a charged particle of unit mass whose position is described by $x$ and is free to move in the interval $(0,\pi)$. The eigenfunctions and energies are

$$\phi_n(x) = \sqrt{\frac{2}{\pi}}\sin(nx) \quad , \quad E_n^{(o)} = \tfrac{1}{2}n^2 \quad (n = 1,2,\cdots) \; . \tag{42}$$

Now suppose a perturbation $V = x - \pi/2$ is applied, corresponding to the energy of the particle in an electric field. The polarizability is $-2E_n^{(2)}$ where $E_n^{(2)}$ is the second-order energy of the nth eigenstate given by an integral similar to (40), namely

$$E_n^{(2)} = -\tfrac{1}{2}\oint_0^{\pi}\left[W_n(z)/\phi_n(z)\right]^2 dz \tag{43}$$

where the contour $C$ from $0$ to $\pi$ avoids the singularities of the integrand at $k\pi/n$ $(k=1,2,\cdots,n-1)$. The function $W_n(z)$ is given by

$$W_n(z) = \frac{1}{\pi}\left[ z(z-\pi) - (z-\tfrac{\pi}{2})\,\frac{\sin(2nz)}{n} + \frac{\sin^2(nz)}{n^2} \right] . \tag{44}$$

When this expression is substituted into (43) and the integration performed analytically ignoring the singularities, we obtain finally

$$E_n^{(2)} = -\frac{1}{24n^2}\left(\frac{15}{n^2} - \pi^2\right) \; . \tag{45}$$

This agrees with the result obtained after much algebraic labour by

summing the usual spectral formula

$$E_n^{(2)} = \sum_{\substack{k=1 \\ (\neq n)}}^{\infty} \frac{V_{nk}^2}{E_n^{(o)} - E_k^{(o)}} \quad . \tag{46}$$

Note that it follows from (46) that

$$\sum_{n=1}^{\infty} E_n^{(2)} = 0 \quad , \tag{47}$$

which can be used to check equation (45).

Removal of Singularities

When the integration is to be carried out numerically by a quadrature designed for integration along the real axis, it is necessary to devise ways of removing the singularities. There are two simple and apparently different ways of doing this, which are however related to each other.

(a) Removal of singularities by subtraction

The function $f_n$ defined by (13) has $n$ simple poles at $a_1,\cdots,a_n$ which may be revealed explicitly by defining a new function $g_n(x)$ by

$$f_n = g_n - \sum_{j=1}^{n} \frac{c_j}{x-a_j} \quad , \tag{48}$$

and choosing the $c_j$ so that $g_n$ is analytic at the points $a_j$. By substituting (48) into the differential equation (22) we get

$$\frac{dg_n}{dx} = \frac{M_n(x)}{\phi_n^2(x)} - \sum_{j=1}^{n} \frac{c_j}{(x-a_j)^2} \quad . \tag{49}$$

The coefficients $c_1,\cdots,c_n$ must therefore by chosen to remove the singularities of $M_n/\phi_n^2$ ; that is

$$c_j = M_n(a_j)/\left[\phi_n'(a_j)\right]^2 \quad (j=1,2,\cdots,n) \quad . \tag{50}$$

Equation (49) may now be integrated along the real x-axis to give

$$g_n(x) = g_n(a) + \int_a^x \left[\frac{M_n(\xi) - \Lambda_n(\xi)}{\phi_n^2(\xi)}\right] d\xi \tag{51}$$

where

$$\Lambda_n(x) = \phi_n^2(x) \sum_{j=1}^{n} \frac{c_j}{(x-a_j)^2} \quad . \tag{52}$$

Similarly equation (40) may be written as an integral along the real axis

$$L_n^{(1)} = -\int_a^b W_n\left[\frac{M_n - \Lambda_n}{\phi_n^2}\right] dx - \sum_{j=1}^{n} c_j \int_a^b \frac{\phi_n(V-V_n)\phi_n}{(x-a_j)}\, dx \quad . \tag{53}$$

In the radial case equation (48) is still valid with the coefficients given by

$$c_j = P_n(a_j)/\left[a_j R_n'(a_j)\right]^2 \quad . \tag{54}$$

The equation corresponding to (41) then becomes

$$L_n^{(1)} = -\int_0^\infty Q_n\left[\frac{P_n - \Gamma_n}{r^2 R_n^2}\right] dr - \sum_{j=1}^{n} c_j \int_0^\infty \frac{r^2 R_n (V-V_n) R_n}{(r-a_j)}\, dr \quad , \tag{55}$$

where

$$\Gamma_n(r) = r^2 R_n^2 \sum_{j=1}^{n} \frac{c_j}{(r-a_j)^2} \quad . \tag{56}$$

(b) Removal of singularities by lower states

An alternative method is to make use of the n eigenfunctions $\phi_0,\cdots,\phi_{n-1}$ for the lower states of the unperturbed system. In place of (13) we write the first-order wave function in the form

$$\chi_n = g_n\phi_n - \sum_{k=0}^{n-1} b_k\phi_k \tag{57}$$

where the coefficients $b_o,\cdots,b_{n-1}$ are constants to be chosen so that $g_n$ is analytic at $a_1,\cdots,a_n$. By substituting (57) for $\chi_n$ into (11) and proceeding as before we get in place of (21)

$$\frac{d}{dx}(\phi_n^2 \frac{dg_n}{dx}) = 2\phi_n(L - L_n)\phi_n - 2\sum_{k=0}^{n-1} b_k(E_k - E_n)\phi_n\phi_k \quad , \tag{58}$$

which on integration gives

$$\phi_n^2 \frac{dg_n}{dx} = M_n(x) - 2\sum_{k=0}^{n-1} b_k(E_k - E_n)\int_a^x \phi_n\phi_k \, d\xi \quad . \tag{59}$$

The second integral may be evaluated immediately by means of the unperturbed Schrödinger equations satisfied by $\phi_k$ and $\phi_n$, namely

$$\left.\begin{aligned} \frac{d^2\phi_k}{dx^2} + 2(E_k - U_o)\phi_k &= 0 \quad , \\ \frac{d^2\phi_n}{dx^2} + 2(E_n - U_o)\phi_n &= 0 \quad . \end{aligned}\right\} \tag{60}$$

By multiplying by $\phi_n$ and $\phi_k$ respectively and subtracting we get

$$\frac{d}{dx}(\phi_k \frac{d\phi_n}{dx} - \phi_n \frac{d\phi_k}{dx}) = 2(E_k - E_n)\,\phi_k\phi_n \quad , \tag{61}$$

and hence by integration

$$\phi_k\phi_n' - \phi_n\phi_k' = 2(E_k - E_n)\int_a^x \phi_k\phi_n \, d\xi \quad . \tag{62}$$

When (62) is substituted into (59) the latter becomes

$$\phi_n^2 \frac{dg_n}{dx} = M_n - \sum_{k=0}^{n-1} b_k(\phi_k\phi_n' - \phi_n\phi_k') \quad . \tag{63}$$

The $n$ coefficients $b_k$ have now to be chosen so that the two terms on the right hand side cancel to the first-order in $(x-a_j)$ at the points $a_j$. This can be achieved if the $b_k$ satisfy the $n$ linear simultaneous equations

$$\sum_{k=0}^{n-1} b_k \phi_k(a_j) = M_n(a_j)/\phi_n'(a_j) \quad (j = 1,\cdots,n) \quad . \tag{64}$$

It follows directly from (61) that the derivative of the right hand side vanishes automatically at the points $a_j$, so that (63) may be integrated along the real axis to give

$$g_n(x) = g_n(a) + \int_a^x \left[\frac{M_n(\xi) - \Omega_n(\xi)}{\phi_n^2(\xi)}\right] d\xi \tag{65}$$

where

$$\Omega_n = \sum_{k=0}^{n-1} b_k(\phi_k\phi_n' - \phi_n\phi_k') \quad . \tag{66}$$

The corresponding formula for $L_n^{(1)}$ is then

$$L_n^{(1)} = -\int_a^b W_n\left[\frac{M_n - \Omega_n}{\phi_n^2}\right] dx - \sum_{k=0}^{n-1} b_k V_{kn} \quad , \tag{67}$$

where

$$V_{kn} = \int_a^b \phi_k V \phi_n \, dx \quad . \tag{68}$$

This form would not be of interest unless it was possible to solve (64) explicitly for the $b_k$ in a large class of cases. The class is that in which the unperturbed functions $\phi_k$ form the basis for a Gauss-type quadrature formula with weight factor $\phi_o^2(x)$. In this case quadrature weights $A_j$ may be found so that

$$\int_a^b \phi_o^2(x)p(x)dx = \sum_{j=1}^{n} A_j \phi_o^2(a_j)p(a_j) \tag{69}$$

exactly for all polynomials $p(x)$ up to degree $2n-1$. The $A_j$ are

given by

$$A_j = \left[\sum_{k=0}^{n-1} \phi_k^2(a_j)\right]^{-1} \tag{70}$$

or alternative formulae[4]. Applying equation (69) to $p = \phi_k\phi_n/\phi_o^2$, we get

$$\sum_{j=1}^{n} A_j\phi_k(a_j)\phi_\ell(a_j) = \delta_{k\ell} \quad (k,\ell = 0,1,\cdots,n-1) \quad . \tag{71}$$

Therefore by multiplying (64) by $A_j\phi_k(a_j)$ and summing over $j$ we get the explicit form

$$b_k = \sum_{j=1}^{n} A_j\phi_k(a_j)M_n(a_j)/\phi_n'(a_j) \quad . \tag{72}$$

The class of functions $\phi_k$ to which this treatment applies is that in which $\phi_k$ is equal to $\phi_o$ times a polynomial of degree $k$ in $x$ (or, more generally, in a transformed variable). Thus it includes the Hermite functions for the simple harmonic oscillator but excludes the Laguerre function solutions of the hydrogen atom.

It will now be shown that in the cases in which this method can be applied it is equivalent to the direct subtraction of the singularities. Consider the expansion of the function $\phi_n(x)/(x-a_j)$ in terms of the complete set of unperturbed functions $\phi_k$. For the class under consideration only the $n$ lowest functions $\phi_o,\cdots,\phi_{n-1}$ are involved so that

$$\phi_n(x)/(x-a_j) = \sum_{k=0}^{n-1} B_k\phi_k(x) \quad , \tag{73}$$

where the $B_k$ are given by

$$B_k = \int_a^b \frac{\phi_k\phi_n}{x-a_j}\,dx \quad . \tag{74}$$

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[4] Z. Kopal, "Numerical Analysis" (Chapman and Hall, London, 1955), chapter 7.

Now the quadrature formula (69) is exact in this case so that

$$B_k = A_j \phi_k(a_j) \phi_n'(a_j) \quad , \tag{75}$$

and therefore

$$\frac{\phi_n(x)}{x-a_j} = A_j \phi_n'(a_j) \sum_{k=0}^{n-1}{}' \phi_k(a_j) \phi_k(x) \quad . \tag{76}$$

Hence from (48) and (50) we have

$$\begin{aligned} \phi_n g_n - \chi_n &= \phi_n \sum_{j=1}^{n}{}' \frac{c_j}{x-a_j} \quad , \\ &= \sum_{j=1}^{n}{}' c_j A_j \phi_n'(a_j) \sum_{k=0}^{n-1}{}' \phi_k(a_j) \phi_k(x) \quad , \\ &= \sum_{k=0}^{n-1}{}' b_k' \phi_k(x) \quad , \end{aligned} \tag{77}$$

where

$$\begin{aligned} b_k' &= \sum_{j=1}^{n}{}' c_j A_j \phi_n'(a_j) \phi_k(a_j) \quad , \\ &= \sum_{j=1}^{n}{}' A_j M_n(a_j) \phi_k(a_j) / \phi_n'(a_j) \quad , \\ &= b_k \end{aligned} \tag{78}$$

by equations (40) and (72). Thus (77) is the same as (57), which proves that in the restricted class of cases under consideration, the two methods are identical; the same arguments apply to the radial equation. While the second method is theoretically interesting in

suggesting that quadrature formulae may be useful in perturbation theory, the first method is quite general and is naturally to be preferred in numerical applications.

Acknowledgment

The authors wish to thank J. B. McLeod (Wadham College, Oxford) for helpful discussion of the analytical solutions.